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(54) Process and catalyst for producing reactor blend polyolefins.

(57) Polyolefin reactor blends obtained by polymerization of ethylene and higher alpha-olefins in the presence of a catalyst system comprising two or more metallocenes and alumoxane.

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PROCESS AND CATALYST FOR PRODUCING REACTOR BLEND POLYOLEFINS

The present invention concerns catalyst and process for the polymerization of ethylene and alpha-olefins. More particularly, the invention relates to catalysts and process for producing (co)polyolefin reactor blends of ethylene and ethylene-alpha-olefin copolymers. The invention further relates to a process for producing tailored (co)polyolefins reactor blends through the proper selections of the catalysts of this invention.

Reactor blends for purposes of this invention are mixtures of two or more polymers of different physical properties (density, melting point, comonomer content, etc.) produced simultaneously in a single polymerization reactor. Catalyst employed in the production of such polymer blends under steady state conditions in one reactor will comprise two or more distinct catalyst components, one predominately catalyzing the formation of one polymer, the other predominately catalyzing the formation of the other polymer.

DESCRIPTION OF THE PRIOR ART

It is known that certain metallocenes such as bis(cyclopentadienyl) titanium and zirconium dialkyls in combination with aluminum alkyl co-catalyst, form homogeneous catalyst systems useful for the polymerization of ethylene. German Patent Application 2,608,863 discloses the use of a catalyst system for the polymerization of ethylene consisting of bis(cyclopentadienyl) titanium dialkyl, aluminum trialkyl and water. German Patent Application 2,608,933 discloses an ethylene polymerization catalyst system consisting of (1) zirconium metallocenes of the general formula  $(\text{cyclopentadienyl})_n\text{ZrY}_{4-n}$ , wherein n stands for a number in the range of 1 to 4, Y for R,  $\text{CH}_2\text{AlR}_2$ ,  $\text{CH}_2\text{CH}_2\text{AlR}_2$  and  $\text{CH}_2\text{CH}(\text{AlR}_2)_2$  wherein R stands for alkyl or metallo alkyl, (2) an aluminum trialkyl cocatalyst and (3) water.

European Patent Appln. No. 0035242 discloses a process for preparing ethylene and atactic propylene polymers in the

1 presence of a halogen-free Ziegler catalyst system of (1)  
2 cyclopentadienyl compound of the formula  
3  $(\text{cyclopentadienyl})_n\text{MeY}_{4-n}$  in which n is an integer from 1  
4 to 4, Me is a transition metal, especially zirconium, and Y is  
5 either hydrogen, a  $\text{C}_1\text{-C}_5$  alkyl or metallo alkyl group or a  
6 compound having the following general formula:  $\text{CH}_2\text{AlR}_2$ ,  
7  $\text{CH}_2\text{CH}_2\text{AlR}_2$  and  $\text{CH}_2\text{CH}(\text{AlR}_2)_2$  in which R represents a  
8  $\text{C}_1\text{-C}_5$  alkyl or metallo alkyl group, and (2) an alumoxane.

9 The above disclosures demonstrate the usefulness of certain  
10 metallocenes in combination with certain aluminum compounds for  
11 the polymerization of ethylene and particularly polymerization  
12 at a high activity rates. The references neither disclose  
13 polyethylene/copolyethylene-alpha-  
14 olefin reactor blends nor methods of producing such reactor  
15 blends.

16 In "Molecular Weight Distribution And Stereoregularity Of  
17 Polypropylenes Obtained With  $\text{Ti}(\text{OC}_4\text{H}_9)_4/\text{Al}(\text{C}_2\text{H}_5)_3$   
18 Catalyst System"; Polymer, Pg. 469-471, 1981, Vol. 22, April,  
19 Doi, et al disclose propylene polymerization with a catalyst  
20 which at about  $41^\circ\text{C}$  obtains a soluble catalyst and insoluble  
21 catalyst fraction, one with "homogeneous catalytic centres" and  
22 the other with "heterogeneous catalytic centres". The  
23 polymerization at that temperature obtains polypropylene having  
24 a bimodal molecular weight distribution.

25 It is also known to produce polymer blends by polymerizing  
26 two or more polymerizable materials in two or more reactors  
27 arranged in series. In accordance with such methods, a  
28 polymerizate is produced in a first reactor which first  
29 polymerizate is passed to a second reactor wherein a second  
30 polymerizate is produced thereby obtaining a blend of the first  
31 and second polymerizates.

32 It is highly desirable to be able to readily and simply  
33 produce blends in a single reactor during which polyethylene  
34 and copolyethylene-alpha-olefins are produced simultaneously.  
35 Not only is a significant reduction in energy costs obtained,  
36 but one obtains a uniform blending of the polymers and one can  
37 simply "tailor" the polymers with respect to molecular weights,

1 weight fraction and the like to obtain blends evidencing  
2 outstanding properties.

3 In view of the foregoing problems, it would be highly  
4 desirable to provide a polymerization catalyst system of  
5 sufficient activity to produce high quality blends of  
6 ethylene-alpha olefin polymers. It is furthermore highly  
7 desirable to be able to produce the blends of ethylene-alpha  
8 olefin polymers directly in a single reactor.

9

10 The present invention provides a process for producing  
11 (co)polyolefin reactor blends comprising polyethylene and  
12 copolyethylene-alpha-olefins. The reactor blends are obtained  
13 directly during a single polymerization process, i.e., the  
14 blends of this invention are obtained in a single reactor by  
15 simultaneously polymerizing ethylene and copolymerizing  
16 ethylene with an alpha-olefin thereby eliminating expensive  
17 blending operations. The invention furthermore provides a  
18 catalyst system for the polymerization of ethylene and ethylene  
19 copolymers simultaneously to provide polyethylene blends. The  
20 process of producing reactor blends in accordance with this  
21 invention can be employed in conjunction with other prior art  
22 blending techniques, for example the reactor blends produced in  
23 a first reactor can be subjected to further blending in a  
24 second stage by use of a series of reactors.

25 Accordingly, there is provided a catalyst system for the  
26 polymerization of reactor blends of polyethylene with  
27 ethylene-alpha-olefin copolymers; said catalyst system  
28 comprising (a) at least two different metallocenes and (b) an  
29 alumoxane. The metallocenes employed in this invention are  
30 organometallic coordination compounds which are  
31 cyclopentadienyl derivatives of a transition metal of Groups  
32 4b, 5b and 6b and include mono, di and tricyclopentadienyls and  
33 their derivatives of the transition metal. The metallocenes  
34 can be represented by the general formula

1  $(C_5R'_m)_pR''_s(C_5R'_m)MeQ_{3-p}$  or  $R''_s(C_5R'_m)MeQ'$ ,  
 2 wherein  $(C_5R'_m)$  is a cyclopentadienyl or substituted  
 3 cyclopentadienyl, each  $R'$ , which can be the same or different,  
 4 is hydrogen or a hydrocarbonyl radical such as alkyl, alkenyl,  
 5 aryl, alkylaryl, or arylalkyl radical having from 1 to 20 carbon  
 6 atoms or two  $R'$  substituents together form a fused  
 7  $C_4-C_6$  ring,  $R''$  is a  $C_1-C_4$  alkylene radical, a dialkyl  
 8 germanium or silicone, or an alkyl phosphine or amine radical  
 9 bridging two  $(C_5R'_m)$  rings,  $Q$  is a hydrocarbon radical such  
 10 as aryl, alkyl, alkenyl, alkylaryl, or arylalkyl radical having  
 11 from 1 to 20 carbon atoms or halogen and each  $Q$  can be the same or  
 12 different,  $Q'$  is an alkylidene radical having from 1 to about  
 13 20 carbon atoms,  $Me$  is a transition metal of Group 4b, 5b, 6b  
 14 of the Periodic Table (Chemical Rubber Company's Handbook of  
 15 Chemistry & Physics, 48th Edition),  $s$  is 0 or 1,  $p$  is 0, 1 or  
 16 2; when  $p = 0$ ,  $s = 0$ ;  $m$  is 4 when  $s$  is 1 and  $m$  is 5 when  $s$  is 0.

17 The ratios of one metallocene to the second metallocene  
 18 will be a function of both the chemical composition of the  
 19 metallocenes as well as the blend being tailored; accordingly,  
 20 the ratio of the two metallocenes can vary greatly and, hence,  
 21 is limited only for the purpose of producing the blends.

22 The present invention also provides a process for producing  
 23 polyolefin reactor blends. The process comprises polymerizing  
 24 ethylene and higher alpha-olefins in the presence of the  
 25 catalyst system described above.

#### 26 DETAILED DESCRIPTION OF THE INVENTION

27 The present invention is directed towards a catalytic  
 28 process for the polymerization of ethylene and one or more  
 29 alpha-olefins to polyethylene-copolyethylene-alpha-olefin  
 30 reactor blends. The polymers are intended for fabrication into  
 31 articles by extrusion, injection molding, thermoforming,  
 32 rotational molding, and the like. In particular, the polymer  
 33 blends of this invention are blends of polyethylenes such as  
 34 high density polyethylene (HDPE) and linear low density  
 35 polyethylene (LLDPE) and with copolyethylene higher  
 36 alpha-olefins having from 3 to about 10 carbon atoms and

preferably 4 to 8 carbon atoms. Illustrative of the higher alpha-olefins are propylene, butene-1, hexene-1 and octene-1. Preferably, the alpha-olefin is propylene or butene-1.

In the process of the present invention, ethylene, together with the alpha-olefins, is polymerized in the presence of a homogeneous catalyst system comprising at least two different metallocenes and an alumoxane.

The alumoxanes are well known in the art and are polymeric aluminum compounds which can be represented by the general formulae  $(R-Al-O)_n$  which is a cyclic compound and  $R(R-Al-O)_nAlR_2$ , which is a linear compound. In the general formula R is a  $C_1-C_5$  alkyl group such as, for example, methyl, ethyl, propyl, butyl and pentyl and n is an integer from 1 to about 20 and preferably from about 1 to about 4. Most preferably, R is methyl and n is 4. Generally, in the preparation of alumoxanes from, for example, aluminum trimethyl and water, a mixture of the linear and cyclic compounds are obtained.

The alumoxane can be prepared in various ways. Preferably, they are prepared by contacting water with solution of aluminum trialkyl, such as, for example, aluminum trimethyl, in a suitable organic solvent such as benzene or an aliphatic hydrocarbon. For example, the aluminum alkyl is treated with water in form of a moist solvent or the aluminum alkyl such as aluminum trimethyl can be desirably contacted with a hydrated salt such as hydrated copper sulfate.

Preferably, the alumoxane is prepared in the presence of a hydrated copper sulfate. The method comprises treating a dilute solution of aluminum trimethyl in, for example, toluene, with copper sulfate represented by the general formula  $CuSO_4 \cdot 5H_2O$ . The ratio of copper sulfate to aluminum trimethyl is desirably about 1 mole of copper sulfate for 5 moles of aluminum trimethyl. The reaction is evidenced by the evolution of methane.

The dual metallocene system usefully employed in accordance with this invention are the mono, di and tricyclopentadienyl or substituted cyclopentadienyl metallocenes and preferably the



1 titanium (IV) and zirconium (IV) metallocenes. The  
 2 metallocenes are represented by the general formula  
 3  $(C_5R'_m)_p R''_s (C_5R'_m)_2 MeQ_{3-p}$  and  
 4  $R''_s (C_5R'_m)_2 MeQ'$  wherein  $(C_5R'_m)$  is cyclopentadienyl  
 5 or substituted cyclopentadienyl, each  $R'$  is the same or  
 6 different and is hydrogen or a hydrocarbyl radical such as  
 7 alkyl, alkenyl, aryl, alkylaryl, or arylalkyl radicals  
 8 containing from 1 to 20 carbon atoms or two carbon atoms are  
 9 joined together to form a  $C_4$ - $C_6$  ring,  $R''$  is a  $C_1$ - $C_4$   
 10 alkylene radical, a dialkyl germanium or silicone, or an alkyl  
 11 phosphine or amine radical bridging two  $(C_5R'_m)$  rings,  $Q$  is  
 12 a hydrocarbyl radical such as aryl, alkyl, alkenyl, alkylaryl,  
 13 or arylalkyl radical having from 1-20 carbon atoms or halogen  
 14 and can be the same or different,  $Q'$  is an alkylidene radical  
 15 having from 1 to about 20 carbon atoms,  $s$  is 0 or 1,  $p$  is 0, 1  
 16 or 2; when  $p$  is 0,  $s$  is 0,  $m$  is 4 when  $s$  is 1 and  $m$  is 5 when  $s$   
 17 is 0 and  $Me$  is a Group 4b, 5b or 6b transition metal and most  
 18 preferably zirconium or titanium.

19 Exemplary hydrocarbyl radicals are methyl, ethyl, propyl,  
 20 butyl, amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl,  
 21 decyl, cetyl, 2-ethylhexyl, phenyl, and the like.

22 Exemplary alkylene radicals are methylene, ethylene,  
 23 propylene, and the like.

24 Preferred examples of substituent  $Q$  are methyl,  
 25 phenyl or chloride.

26 Exemplary halogen atoms include chlorine, bromine  
 27 and iodine and of these halogen atoms, chlorine is  
 28 preferred.

29 Exemplary of the alkylidene radicals are methylenidene,  
 30 ethylenidene and propylenidene.

31 Preferably the catalyst comprises at least two  
 32 zirconocenes or at least one titanocene and at least one  
 33 zirconocene.

34 Illustrative but non-limiting examples of the titano-  
 35 cenes which can be usefully employed in accordance with  
 36 this invention are bis(cyclopentadienyl) titanium

- 1 diphenyl, the carbene represented by the formula
- 2  $\text{Cp}_2\text{Ti}=\text{CH}_2 \cdot \text{Al}(\text{CH}_3)_2\text{Cl}$ , and derivatives of this
- 3 reagent such as  $\text{Cp}_2\text{Ti}=\text{CH}_2 \cdot \text{Al}(\text{CH}_3)_3$ ,
- 4  $(\text{Cp}_2\text{TiCH}_2)_2$ ,  $\text{Cp}_2\text{TiCH}_2\text{CH}(\text{CH}_3)\text{CH}_2$ ,
- 5  $\text{Cp}_2\text{Ti}=\text{CHCH}_2\text{CH}_2$ ,  $\text{Cp}_2\text{Ti}=\text{CH}_2 \cdot \text{AlR}'_2\text{Cl}$ , wherein Cp
- 6 is a cyclopentadienyl or substituted cyclopentadienyl
- 7 radical,

1 and R''' is an alkyl, aryl or alkylaryl radical having from  
 2 1-18 carbon atoms; substituted bis(Cp)Ti(IV) compounds such as  
 3 bis(indenyl)Ti diphenyl or dichloride,  
 4 bis(methylcyclopentadienyl)Ti diphenyl or dihalides and other  
 5 dihalide complexes; dialkyl, trialkyl, tetra-alkyl and  
 6 penta-alkyl cyclopentadienyl titanium compounds such as  
 7 bis(1,2-dimethylcyclopentadienyl)Ti diphenyl or dichloride,  
 8 bis(fluorenyl)Ti dichloride, bis(1,2-diethylcyclopentadienyl)Ti  
 9 diphenyl or dichloride and other dihalide complexes; silicone,  
 10 phosphine, amine or carbon bridged cyclopentadiene complexes,  
 11 such as dimethyl silyldicyclopentadienyl titanium diphenyl or  
 12 dichloride, methyl phosphine dicyclopentadienyl titanium  
 13 diphenyl or dichloride, methylenedicyclopentadienyl titanium  
 14 diphenyl or dichloride and other dihalide complexes.

15 Illustrative but non-limiting examples of the zirconocenes  
 16 which can be usefully employed in accordance with this  
 17 invention are bis(cyclopentadienyl)zirconium diphenyl,  
 18 bis(cyclopentadienyl)zirconium dimethyl; the alkyl substituted  
 19 cyclopentadienes, such as bis(ethyl cyclopentadienyl)zirconium  
 20 dimethyl, bis( $\beta$ -phenylpropylcyclopentadienyl)zirconium  
 21 dimethyl, bis(methylcyclopentadienyl)zirconium dimethyl and  
 22 dihalide complexes of the above; di-alkyl, tri-alkyl,  
 23 tetra-alkyl, and penta-alkyl cyclopentadienes, such as  
 24 bis(pentamethylcyclopentadienyl)zirconium dimethyl, bis  
 25 (1,2-dimethylcyclopentadienyl)zirconium dimethyl,  
 26 bis(1,3-diethylcyclopentadienyl)zirconium dimethyl and dihalide  
 27 complexes of the above; silicone, phosphorus, and carbon  
 28 bridged cyclopentadiene complexes such as  
 29 dimethylsilyldicyclopentadienyl zirconium dimethyl or dihalide,  
 30 methylphosphine dicyclopentadienyl zirconium dimethyl or  
 31 dihalide, and methylene dicyclopentadienyl zirconium dimethyl  
 32 or dihalide, carbenes represented by the formulae  
 33  $\text{Cp}_2\text{Zr}=\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2\text{CH}_3$ , and derivatives of these  
 34 compounds such as  $\text{Cp}_2\text{ZrCH}_2\text{CH}(\text{CH}_3)\text{CH}_2$ .

35 The ratio of aluminum in the alumoxane to total metal in  
 36 the metallocenes can be in the range of 0.5:1 to  
 37  $10^5$ :1, and preferably 5:1 to 1000:1. The molar

1 ratio of the metallocenes can vary over a wide range and in  
2 accordance with this invention the molar ratios are controlled  
3 by the product polymer blend desired.

4 The reactivity ratios of the metallocenes in general are  
5 obtained by methods well known such as, for example, as  
6 described in "Linear Method for Determining Monomer Reactivity  
7 Ratios in Copolymerization", M. Fineman and S. D. Ross, J.  
8 Polymer Science 5, 259 (1950) or "Copolymerization", F. R. Mayo  
9 and C. Walling, Chem. Rev. 46, 191 (1950) incorporated herein  
10 in its entirety by reference. For example, to determine  
11 reactivity ratios the most widely used copolymerization model  
12 is based on the following equations:

$$13 \quad M_1^* + M_1 \xrightarrow{k_{11}} M_1^* \quad (1)$$

$$14 \quad M_1^* + M_2 \xrightarrow{k_{12}} M_2^* \quad (2)$$

$$15 \quad M_2^* + M_1 \xrightarrow{k_{21}} M_1^* \quad (3)$$

$$16 \quad M_2^* + M_2 \xrightarrow{k_{22}} M_2^* \quad (4)$$

17 where  $M_i$  refers to a monomer molecule which is arbitrarily  
18 designated  $i$  (where  $i = 1, 2$ ) and  $M_i^*$  refers to a growing  
19 polymer chain to which monomer  $i$  has most recently attached.

20 The  $k_{ij}$  values are the rate constants for the indicated  
21 reactions. Thus,  $k_{11}$  represents the rate at which an  
22 ethylene unit inserts into a growing polymer chain in which the  
23 previously inserted monomer unit was also ethylene. The  
24 reactivity rates follow as:  $r_1 = k_{11}/k_{12}$  and  $r_2 =$   
25  $k_{22}/k_{21}$  wherein  $k_{11}$ ,  $k_{12}$ ,  $k_{22}$  and  $k_{21}$  are the rate  
26 constants for ethylene (1) or propylene (2) addition to a  
27 catalyst site where the last polymerized monomer is an  
28 ethylene ( $k_{1x}$ ) or propylene ( $k_{2x}$ ).

29 In Table I the ethylene-propylene reactivity rates  $r_1$  and  
30  $r_2$  are listed for several metallocenes. It can be seen that  
31 with increased steric interaction at the monomer coordination  
32 site  $r_1$  increases, i.e. the tendency for ethylene  
33 polymerization increases over propylene polymerization.

1 It can be seen from Table I that if one desires a blend  
 2 comprising HDPE/ethylene-propylene copolymer one would select  
 3 bis(pentamethylcyclopentadienyl)ZrCl<sub>2</sub> and  
 4 bis(cyclopentadienyl)Ti diphenyl or  
 5 dimethylsilyldicyclopentadienyl zirconium dichloride in ratios  
 6 of 5:1 to 1:1 whereas if one desires a blend  
 7 comprising LLDPE/ethylene-propylene one would select  
 8 bis(cyclopentadienyl)Zr dimethyl or  
 9 bis(methylcyclopentadienyl)ZrCl<sub>2</sub> and bis(cyclopentadienyl)Ti  
 10 diphenyl or dimethylsilyldicyclopentadienyl ZrCl<sub>2</sub> in ratios  
 11 of 10:1 to 1:1.

12 Desirably, the metallocene molar ratio will be 100:1  
 13 to 1:100, and preferably 10:1 to 1:10. The  
 14 specific metallocenes selected and their molar ratios are  
 15 depended upon the molecular composition desired for the  
 16 component polymers and the overall composition desired for the  
 17 blend. In general, the component catalyst used in a reactor  
 18 blend catalyst mixture will each have r values which are  
 19 different in order to produce final polymer compositions which  
 20 comprise blends of two or more polymers.

TABLE I

22	Catalyst	$r_1$	$r_2$
23	Cp <sub>2</sub> Ti=CH <sub>2</sub> · Al(Me) <sub>2</sub> Cl	24	0.0085
24	Cp <sub>2</sub> TiPh <sub>2</sub>	19.5±1.5	0.015±.002
25	Me <sub>2</sub> SiCp <sub>2</sub> ZrCl <sub>2</sub>	24±2	0.029±.007
26	Cp <sub>2</sub> Zr·Cl <sub>2</sub>	48±2	0.015±.003
27	(MeCp) <sub>2</sub> ZrCl <sub>2</sub>	60	
28	(Me <sub>5</sub> Cp) <sub>2</sub> ZrCl <sub>2</sub>	250±30	.002±0.001
29	[Cp <sub>2</sub> ZrCl] <sub>2</sub> O	50	0.007

30 The solvents used in the preparation of the catalyst system  
 31 are inert hydrocarbons, in particular a hydrocarbon that is  
 32 inert with respect to the catalyst system. Such solvents are  
 33 well known and include, for example, isobutane, butane,  
 34 pentane, hexane, heptane, octane, cyclohexane,  
 35 methylcyclohexane, toluene, xylene and the like.

1       The catalyst systems described herein are suitable for  
2     producing polymer product blends in solution, slurry or a gas  
3     phase polymerizations and over a wide range of temperatures and  
4     pressures. For example, such temperatures may be in the range  
5     of -60 to 280°C and especially in the range of  
6     50 to 160°C. The pressures employed in the  
7     process of the present invention are those well known for  
8     example, in the range of 1 to 500 atmospheres and  
9     greater.

10    In a solution phase polymerization the alumoxane and  
11    metallocene can be employed as a homogeneous catalyst system.  
12    The alumoxane is preferably dissolved in a suitable solvent,  
13    typically in inert hydrocarbon solvent such as toluene, xylene,  
14    and the like in molar concentrations of 0.1 to 3.0,  
15    however greater or lesser amounts can be employed.

16       The soluble metallocenes can be converted to supported  
17    heterogeneous catalyst by depositing said metallocenes on  
18    typical catalyst supports such as, for example, silica,  
19    alumina, and polyethylene. The solid catalysts in combination  
20    with an alumoxane can be usefully employed in slurry and gas  
21    phase olefin polymerizations.

22       After polymerization and deactivation of the catalyst, the  
23    product polymer blend can be recovered by processes well known  
24    in the art for removal of deactivated catalysts and solution.  
25    The solvents may be flashed off from the polymer solution and  
26    the polymer obtained extruded into water and cut into pellets  
27    or other suitable comminuted shapes.

28       Pigments, antioxidants and other additives, as is known in  
29    the art, may be added to the polymer.

30       The polymer product obtained in accordance with this  
31    invention will have a weight average molecular weight in the  
32    range of 500 to 2,000,000 and preferably 10,000 to  
33    500,000. The component polymers in the reactor blend can  
34    have the same or different average molecular weights and  
35    comonomer composition; however, it is preferable for most end  
36    uses that the average molecular weights and comonomer  
37    composition be different.

1 Illustrative, but nonlimiting examples of reactor blends  
2 which can be produced in accordance with this invention are  
3 HDPE/EPR copolymer, LLDPE/EPR copolymer, HDPE/LLDPE and  
4 HDPE/LLDPE/EPR copolymer blends. These polymers demonstrate  
5 superior properties such as for example impact resistance and  
6 tear strength and process more easily than the individual  
7 component polymers.

8 The polymers produced by the process of this present  
9 invention are capable of being fabricated into a wide variety  
10 of articles, as is known for blend of ethylene and copolymers  
11 of ethylene and higher alpha-olefins. The present invention is  
12 illustrated by the following examples.

### 13 EXAMPLES

14 In the examples following the molecular weights were  
15 determined on a Water's Associates Model No. 150C GPC. The  
16 measurements were made by dissolving polymer samples in hot  
17 trichlorobenzene (TCB) and filtered. The GPC (Gel Permeation  
18 Chromotography) runs were performed at 145°C in TCB at 1.5  
19 ml/min using two Shodex A80M/S columns of 9.4 mm internal  
20 diameter from Perkins Elmer Inc. 300 milliliter of 3.1 percent  
21 solutions in TCB were injected and the chromatographic runs  
22 monitored at sensitivity equal -64 and scale factor equal 65.  
23 The samples were run in duplicate. The integration parameters  
24 were obtained with a Water's Associates data module. An  
25 antioxidant, N-phenyl-2-naphthylamine, was added to all samples.

26 In the examples following the alumoxane was prepared in the  
27 following manner:

28 600cc of a 14.5% solution of trimethylaluminum (TMA) in  
29 heptane was added in 30cc increments at 5 minute intervals,  
30 with rapid stirring, to 200cc toluene in a Zipperclave reactor  
31 under nitrogen and maintained at 100°C. Each increment was  
32 immediately followed by the addition of 0.3cc water. The  
33 reactor was vented of methane after each addition. Upon  
34 completion of the addition, the reactor was stirred for 6 hours  
35 while maintaining the temperature at 100°C. The mixture,

1 containing soluble alumoxane is allowed to cool to room  
2 temperature and settle. The clear solution containing the  
3 soluble alumoxane is separated by decantation from the solids.

4  
5 Example 1(a) - Reactor blend

6 A 1-liter stainless steel pressure vessel, equipped with an  
7 incline blade stirrer, an external water jacket for temperature  
8 control, a septum inlet and vent line, and a regulated supply  
9 of dry ethylene, propylene and nitrogen, was dried and  
10 deoxygenated with a nitrogen flow. 400cc of dry, degassed  
11 toluene was introduced directly into the pressure vessel. 25cc  
12 of 0.64 molar (in total aluminum) alumoxane was injected into  
13 the vessel by a gas tight syringe through the septum inlet and  
14 the mixture was stirred at 1,200 rpms and 50°C for 5 minutes  
15 at zero (0) psig of nitrogen. 1.12 mg bis(cyclopentadienyl)  
16 titanium phenyl dissolved in 2.0 ml of dry, distilled toluene  
17 was injected through the septum inlet into the vessel.  
18 Similarly, 0.107 mg. bis(pentamethylcyclopentadienyl) zirconium  
19 dimethyl in 2.0 ml dry, distilled toluene was injected. The  
20 solution was saturated with 200cc propylene at a pressure of  
21 165 psig. Thereafter ethylene at 25 psig was passed into the  
22 vessel for 60 minutes while maintaining the temperature at  
23 50°C at which time the reaction was stopped by rapidly  
24 venting and cooling. The copolymer was evaporated to dryness,  
25 weighed and analyzed by GPC and IR. 62 gms of a blend of  
26 polyethylene and EPR copolymer which analyzed for 6 mole %  
27 propylene and having a  $\bar{M}_n$  of 16,500 and a  $\bar{M}_w$  of 41,800 was  
28 recovered.

29 Example 1(b) - Use of One Metallocene -

30 bis(pentamethylcyclopentadienyl)Zirconiumdimethyl

31 A 1-liter stainless steel pressure vessel, equipped with an  
32 incline blade stirrer, an external water jacket for temperature  
33 control, a septum inlet and vent line, and a regulated supply  
34 of dry ethylene, propylene and nitrogen, was dried and  
35 deoxygenated with a nitrogen flow. 400cc of dry, degassed



1 toluene was introduced directly into the pressure vessel. 25cc  
2 of 0.64 molar (in total aluminum) alumoxane was injected into  
3 the vessel by a gas tight syringe through the septum inlet and  
4 the mixture was stirred at 1,200 rpms and 50°C for 5 minutes  
5 at zero (0) psig of nitrogen. 0.122 mg  
6 bis(pentamethylcyclopentadienyl)zirconium dimethyl dissolved in  
7 2.0 ml of dry, distilled toluene was injected through the  
8 septum inlet into the vessel. Liquid propylene (200cc) was  
9 added from a calibrated addition vessel resulting in a  
10 propylene pressure of 153 psig. Thereafter ethylene at 25 psig  
11 was passed into the vessel for 90 minutes while maintaining the  
12 temperature at 50°C at which time the reaction was stopped by  
13 rapidly venting and cooling. 76 gms of polyethylene which  
14 analyzed for 3.4% propylene and having a  $\bar{M}_n$  of 15,300 and a  $\bar{M}_w$   
15 of 36,400 was recovered. The analysis was performed as in  
16 Example 1(a).

17 Example 1(c) - Use of One Metallocene -

18 bis(cyclopentadienyl)Titanium phenyl

19 A 1-liter stainless steel pressure vessel, equipped with an  
20 incline blade stirrer, an external water jacket for temperature  
21 control, a septum inlet and vent line, and a regulated supply  
22 of dry ethylene, propylene and nitrogen, was dried and  
23 deoxygenated with a nitrogen flow. 400cc of dry, degassed  
24 toluene was introduced directly into the pressure vessel. 25cc  
25 of 0.64 molar (in total aluminum) alumoxane was injected into  
26 the vessel by a gas tight syringe through the septum inlet and  
27 the mixture was stirred at 1,200 rpms and 50°C for 5 minutes  
28 at zero (0) psig of nitrogen. 1.04 mg bis(cyclopentadienyl)  
29 titanium phenyl dissolved in 2.0 ml of dry, distilled toluene  
30 was injected through the septum inlet into the vessel. Liquid  
31 propylene (200cc) was added from a calibrated addition vessel  
32 resulting in a propylene pressure of 165 psig. Thereafter  
33 ethylene at 25 psig was passed into the vessel for 90 minutes  
34 while maintaining the temperature at 50°C at which time the  
35 reaction was stopped by rapidly venting and cooling. 14.4 gms  
36 of polyolefin which analyzed for 65% ethylene and 35% propylene

1 and having a  $\bar{M}_n$  of 45,400 and a  $\bar{M}_w$  of 137,000 was recovered.  
2 The analysis was performed as in Example 1(a).

3 Example 2 - Use of Two Different Metallocenes

4 A 1-liter stainless steel pressure vessel, equipped with an  
5 incline blade stirrer, an external water jacket for temperature  
6 control, a septum inlet and vent line, and a regulated supply  
7 of dry ethylene, propylene and nitrogen, was dried and  
8 deoxygenated with a nitrogen flow. 400cc of dry, degassed  
9 toluene was introduced directly into the pressure vessel.  
10 10.0cc of 0.83 molar (in total aluminum) alumoxane was injected  
11 into the vessel by a gas tight syringe through the septum inlet  
12 and the mixture was stirred at 1,200 rpms and 80°C for 5  
13 minutes at zero (0) psig of nitrogen. 2.127 mg  
14 bis(pentamethylcyclopentadienyl) zirconium dichloride dissolved  
15 in 2.0 ml of dry, distilled toluene was injected through the  
16 septum inlet into the vessel. Similarly, 0.2628 mg  
17 bis(methylcyclopentadienyl) zirconium dichloride in 0.25 ml  
18 dry, distilled toluene was injected. The solution was  
19 saturated with propylene at a pressure of 111 psig for 15  
20 seconds. Thereafter ethylene at 15 psig was passed into the  
21 vessel for 20 minutes while maintaining the temperature at  
22 80°C and the pressure at 126° psig at which time the  
23 reaction was stopped by rapidly venting and cooling. 18.0 gms  
24 of a blend of PE and EPR copolymer analyzed for 7.1 mole %  
25 propylene and having a  $\bar{M}_n$  of 2,000 and a  $\bar{M}_w$  of 8,300 was  
26 recovered. A fractionation analysis was performed by stirring  
27 a 10 g portion of this solid product for one hour in 100 ml of  
28 toluene. The slurry was filtered and washed with 10 ml of  
29 fresh toluene. The copolymer in solution and the solid product  
30 were separately evaporated to dryness, weighed and analyzed by  
31 GPC and IR.

32 The soluble product (7.0g) had a  $\bar{M}_n$  of 2,200 and a  $\bar{M}_w$  of  
33 11,900 and analyzed for 30 mole % propylene. The insoluble  
34 fraction had an  $\bar{M}_n$  of 3000 and a  $\bar{M}_w$  of 7,400 and analyzed to  
35 contain 4.8% propylene.

Example 3

A 1-liter stainless steel pressure vessel, equipped with an incline blade stirrer, an external water jacket for temperature control, a septum inlet and vent line, and a regulated supply of dry ethylene, propylene and nitrogen, was dried and deoxygenated with a nitrogen flow. 400cc of dry, degassed toluene was introduced directly into the pressure vessel. 10cc of alumoxane molar (8.3 m moles in total aluminum) was injected into the vessel by a gas tight syringe through the septum inlet and the mixture was stirred at 1,200 rpms and 50°C for 5 minutes at zero (0) psig of nitrogen. 0.539 mg bis(methylcyclopentadienyl) zirconium dimethyl dissolved in 2.0 ml of dry, distilled toluene was injected through the septum inlet into the vessel. Similarly, 1.03 mg bis(pentamethylcyclopentadienyl) zirconium dichloride in 2.0 ml dry, distilled toluene was injected. The solution was saturated with 200cc propylene at a pressure of 111 psig for 15 seconds. Thereafter ethylene at 25 psig ( $C_3/C_2$  liquid ratio = 16) was passed into the vessel for 20 minutes while maintaining the temperature at 50°C at which time the reaction was stopped by rapidly venting and cooling. 30.0 gms of a blend of LLDPE and EP copolymer analyzed for 3.6% propylene and having a  $\bar{M}_n$  of 5,600 and a  $\bar{M}_w$  of 17,300 was recovered. The fractionation analysis, GPC & IR performed as in Example 2 yielded 3.0 gms of a soluble fraction having a  $\bar{M}_n$  of 3,500, a  $\bar{M}_w$  of 16,000 and mole % of  $C_3^=$  of 20.6. The insoluble fraction (7.0 gms) had a  $\bar{M}_n$  of 5,400, a  $\bar{M}_w$  of 16,400 and mole %  $C_3^=$  of 2.9%.

CLAIMS:

1. A catalyst system for the production of reactor blend polymers, said catalyst comprising (a) at least two different organometallic coordination compounds which are derivatives of mono, di or tricyclopentadienyls with Group 4b, 5b and 6b transition metal, the compounds having different reactivity with respect to the monomers employed and (b) an alumoxane.

2. A homogeneous catalyst system for the production of reactor blend polymers comprising a blend of polyethylene and an ethylene-olefin copolymer; said catalyst comprising:

(a) at least two metallocenes having represented by the general formula

$(C_5R'_p)R''_s(C_5R'_m)MeQ_{3-p}$  or  $R''_s(C_5R'_m)_2MeQ'$  each having different reactivity ratios, and

(b) an alumoxane

wherein  $(C_5R'_m)$  is a cyclopentadienyl or substituted cyclopentadienyl, each  $R'$  which can be the same or different is hydrogen or a hydrocarbyl radical or two  $R'$  substituents together form a fused  $C_4-C_6$  ring,  $R''$  is a  $C_1-C_4$  alkylene radical, a dialkyl germanium or silicone, or an alkyl phosphine or amine radical bridging two  $(C_5R'_m)$  rings,  $Q$  is a hydrocarbon radical or halogen and can be the same or different,  $Q'$  is an alkylidene radical having from 1 to 20 carbon atoms,  $Me$  is a transition metal of Group 4b, 5b and 6b,  $s$  is 0 or 1,  $p$  is 0, 1 or 2; when  $p = 0$ ,  $s = 0$ ;  $m$  is 4 when  $s$  is 1;  $m$  is 5 when  $s$  is 0.

3. The catalyst system of claim 2 wherein  $Q$  is methyl, phenyl or chloride.

4. The catalyst system of claim 2 or claim 3, wherein Me is selected from zirconium and titanium.

5. The catalyst system of claim 4 comprising at least 2 zirconocenes.

6. The catalyst system of claim 4 comprising at least 1 titanocene and 1 zirconocene.

7. The catalyst system of claim 5 comprising bis (methylcyclopentadienyl) zirconium dichloride and bis (penta-methylcyclopentadienyl) zirconium dichloride.

8. A process for producing a reactor blend comprising polymerizing ethylene and at least alpha-olefin simultaneously in the presence of the catalyst system of any of claims 1 to 7.

9. The process of claim 8 wherein the polymer blend comprises a blend of polyethylene and copolyethylene-propylene.

10. The process of claim 9 wherein the polyethylene is LLDPE or HDPE.



European Patent  
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# EUROPEAN SEARCH REPORT

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Application number

EP 84 30 3806

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
A	EP-A-0 069 951 (HOECHST) * Claims 1-8 *	1	C 08 F 10/00 C 08 F 4/62
A,D	EP-A-0 035 242 (HANSJÖRG SINN) * Claims 1,2 *	1	
A	GB-A- 978 893 (HOECHST) * Claims 1,5,7; page 2, lines 26-33 *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 7)
			C 08 F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 13-09-1984	Examiner WEBER H.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	